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## KINETICS OF SOLID-STATE REACTIONS IN Ni-Zr THIN FILMS

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### ABSTRACT

We have studied the kinetics of the solid-state amorphizing reaction in thin film multilayers of Ni and Zr. Crystalline Ni and Zr films were deposited in ultra-high vacuum onto platinum resistance thermometers embedded in alumina. An electronic feedback circuit controls the temperature of the substrata by adjusting the power dissipated by the platinum resistors. We find that structural relaxation in the as-deposited Ni and Zr films affects the initial stages of the reaction. For long reaction times there is a discontinuous change in the reaction rate. The time to reach this transition increases with film thickness and depends exponentially on  $1/T$ , with an apparent activation energy of 3 eV atom<sup>-1</sup>.

### INTRODUCTION

A solid-state amorphizing reaction (SSAR) has been shown to occur [1,2] at the interfaces of two pure metals A and B having the following characteristics: (1) metals A and B have a large negative heat of mixing in the amorphous state and (2) metals A and B have vastly different diffusivities in each other and in the amorphous alloy to be formed. The first condition provides the thermodynamic driving force for the reaction, whereas the second condition ensures that the SSAR is kinetically favored over the nucleation and growth of crystalline phases.

Measurements of the SSAR kinetics in early and late transition metal multilayers [3,4,5,6] have identified three regimes. For short annealing times the reaction rate is low. Data in this region are sparse because of the difficulty in bringing the multilayers to the reaction temperature within a short time interval. However, Rutherford backscattering (RBS) [7,8] and resistivity measurements [9,10] suggest that there is a time delay for the initiation of the reaction and this delay has been taken as evidence for an interfacial reaction barrier. Other possible explanations for the initial delay in the SSAR are based on grain growth [11] and the release of mechanical stresses [12] in the films. Both mechanisms would produce changes in the film properties during the initial stage of annealing.

For intermediate times the amorphous layer thickness increases proportionally to  $t^{1/2}$ . It is well established that for this regime the SSAR rate is limited by the diffusion of the smaller late transition atom in the amorphous layer already formed [13,14,15].

For long reaction times, the kinetics change again, showing a decreased reaction rate. This third stage has been attributed to the exhaustion of crystalline material [16], formation of Kirkendall voids [11], relief of mechanical stress [17,18], and to the establishment of the terminal solubility in the early transition metal [8].

We present measurements of the SSAR kinetics in vacuum-deposited thin film multilayers of nickel and zirconium. To study the early stages of the reaction we developed a substrate system of fast thermal response and high stability. The reaction kinetics are deduced from resistivity measurements obtained during isothermal and constant-heating-rate annealings.

## EXPERIMENTAL

The multilayers are deposited onto alumina substrata which incorporate a platinum thin film resistor. These resistance thermometers [19] are 0.125" x 0.400" x 0.030" and weigh 90 mg. The substrate surface on which the films are deposited is polished with 0.25  $\mu$ m diamond paste. A pad of tungsten, 2.5 mm long and 150 nm thick, is then vacuum deposited onto either end of this surface. These pads are used as electrical contacts to measure the resistance of the Ni/Zr films using a 4-point AC technique. Tungsten was chosen because of its low diffusivity in both crystalline zirconium and amorphous NiZr alloy [20,21]. The current and voltage leads are 0.001" diameter platinum wires, which are laid across the tungsten pads and attached with a thin coating of colloidal graphite. Low thermal conductivity fiberglass straps are used to hold the substrate in the vacuum chamber. Each assembly is baked in situ for at least 20 h at 700°C to remove adsorbed water.

The resistor is connected as one arm of a Wheatstone bridge, the other three arms are resistors with a near-zero temperature coefficient of resistance. For the platinum resistor,  $(1/R)(dR/dT) = 0.00385 \text{ } ^\circ\text{C}^{-1}$ . An electronic feedback circuit [22] detects any imbalance in the bridge and increases or decreases the voltage applied to the bridge accordingly. An increase in the applied voltage increases the power dissipated by the platinum resistor and thus increases its temperature and resistance. Because of the low thermal mass of the resistor, thermal equilibrium following a change in the set point is achieved within a few seconds. Notice that there is no need for a separate heater and thermometer because the platinum resistor fulfills both requirements.

The substrata were heated repeatedly to 700°C without hysteresis error. The accuracy of the temperature measurement was verified by measuring the resistance of a vacuum-deposited 85 nm-thick nickel film during heating at a constant rate of 10 K min<sup>-1</sup>. A clear change in  $dR/dT$  occurs at 358°C which corresponds to the Curie temperature of nickel [23]. The present thermal system represents a substantial improvement in the accuracy of surface temperature measurements. To demonstrate this point, we also measured the temperature of the nickel film by attaching a 0.001" diam. Pt/Pt-10% Rh thermocouple (the thinnest we could work with) to the nickel film using the colloidal graphite. For a substrate temperature of 300°C the thermocouple measured only 289°C, with the error increasing for higher set temperatures. Errors of this magnitude cannot be neglected when studying reaction kinetics, which depend exponentially on temperature. Even larger errors are expected when heating, in vacuum, ceramic or glass substrata which are held by simple mechanical contact against a metal block of known temperature.

## RESULTS

### Constant Heating Rate Measurements

The Ni/Zr multilayers were prepared by electron-beam evaporation in ultra-high vacuum. The base pressure was below  $1 \times 10^{-9}$  torr and during deposition rose to  $5 \times 10^{-8}$  torr. The resistance measurements were made in situ at pressures below  $10^{-10}$  torr.

Figure 1 shows the electrical resistance of a five-film Ni/Zr multilayer heated at  $10 \text{ K min}^{-1}$ . The changes in resistance reflect the following transformations. From (a) to (b) the temperature is too low for significant interdiffusion; the resistance increases linearly with temperature, as expected for pure crystalline metals. At (b), the Ni becomes sufficiently mobile for the SSAR to begin at each Ni-Zr interface. Because the amorphous alloy has a higher resistance than the pure metals from which it is formed, the resistance of the multilayer increases. The SSAR is completed at (c) when the supply of one or both pure metals is exhausted. From (c) to (d) the resistance is approximately constant, in agreement with the observation that the resistance of amorphous alloys is largely temperature independent. Crystallization of the amorphous alloy begins at (d), decreasing the multilayer resistance. At (e), crystallization is completed; the alloy has a stable structure which is unaffected by further temperature variations (e to f to g to f).

Figure 2 shows the electrical resistivity of three multilayers heated at the constant rate of  $10 \text{ K min}^{-1}$ . The middle curve reproduces the data in Fig. 1. The remaining two curves are for multilayers having individual film thicknesses twice and half those for the middle curve, respectively. Solid curves have been drawn through the crystallization temperature and the temperature at which the SSAR is completed. As expected for fully reacted films, the crystallization temperature is independent of film thickness. The temperature at which the SSAR is completed increases with increasing film thickness. An extrapolation of these two curves to an intersection suggests that the maximum amorphous layer thickness that can be formed at the heating rate of  $10 \text{ K min}^{-1}$  is approximately 150 nm. This value is slightly higher than the limiting value of 100 nm found by Meng et al. [24] during isothermal SSARs.

Region (b) to (c) of Fig. 1 can be used to derive the diffusivity of nickel in the amorphous alloy. In a separate paper [15] we developed a simple model to relate the measured resistance  $R_{\text{meas}}$  to amorphous layer thickness  $X_{\text{am}}$ :

$$\frac{X_{\text{am}}}{d} = \frac{1/R_{\text{meas}} - 1/R_i}{1/R_f - 1/R_i} \quad (1)$$

where  $d$  is the total multilayer thickness, and  $R_i$  and  $R_f$  are the initial and final film resistances, respectively. A curve of  $X_{\text{am}}$  vs  $T$  can then be used to determine the diffusivity of Ni from the relation [15]:

$$\ln \left( X_{\text{am}} \cdot \frac{dX_{\text{am}}}{X_{\text{am}}} \right) = \ln(CD^0_{\text{Ni}}) - \frac{E}{kT} \quad (2)$$

Figure 3 is a plot of the left hand side of Eq. (2) versus  $1000/T$ . Data for three

multilayers of Fig. 2 are included. Also shown is the data for a multilayer identical to 2X, but which was annealed at  $2 \text{ K min}^{-1}$ . A least squares fit to the linear portion of samples 1X, 2X, and 4X gives the values  $D_{\text{Ni}}^0 = (2.5 \pm 4) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $E = 1.01 \pm 0.04 \text{ eV atom}^{-1}$ .

### Isothermal Measurements

We have examined the various kinetic regimes in SSARs by resistance measurements made on bilayer samples during isothermal annealing. The films were deposited with the substrata kept at ambient temperature. Following deposition, the set point of the substrate temperature controller was increased in one step and a stable reaction temperature was reached within 20 s.

The curves in Figs. 4 - 6 identify three kinetics regimes labeled (a), (b), and (c) [Notice the different scales for the abscissa]. The temperature dependence of regime (a) changes with annealing temperature; whereas for  $300^\circ\text{C}$  (Fig. 4)  $1/R$  in regime (a) has a  $t^{1/2}$  dependence, at  $350^\circ\text{C}$  (Fig. 6)  $1/R$  versus  $t^{1/2}$  has a clear convex curvature. One possible explanation for this convex dependence is that the resistance of the unreacted Ni and Zr films changes concurrently with the SSAR taking place at the Ni/Zr interface. To check this, we annealed a 400 nm-thick zirconium film at  $330^\circ\text{C}$ . The change in  $1/R$  of the as-deposited film is shown in Fig. 7 as a function of  $t^{1/2}$ , where  $t$  is the time from the end of the deposition. Although a measurement has not been made, a similar change in  $1/R$  is expected to occur in the nickel films following deposition.

The intermediate regime, (b), is characterized by a linear  $t^{1/2}$  dependence which can be clearly seen in Figs. 4 and 5. This time dependence has been discussed earlier. At the highest reaction temperature of  $350^\circ\text{C}$  (Fig. 6), regime (b) becomes narrow and there seems to be a continuous transition from regime (a) to (c).

The transition between regimes (b) and (c) is defined as the annealing time,  $t_0$ , at which  $1/R$  deviates from a  $t^{1/2}$  dependence. We investigated the dependence of  $t_0$  on film thickness and reaction temperature. For the former, we reacted three bilayers, having thicknesses in the ratios of 1:2:4, at  $330^\circ\text{C}$ . Although the data in Fig. 8 are not sufficient to discern the analytical dependence of  $t_0(x)$ , they do show that  $t_0$  increases with increasing  $x$ . The dependence of  $t_0$  on temperature was investigated on bilayers of constant thickness. Figure 9 shows that  $t_0$  is linearly dependent on  $1000/T$ , suggesting that  $t_0$  is determined by a thermally activated process with an activation energy close to  $3 \text{ eV atom}^{-1}$ .

### DISCUSSION

Platinum resistance thermometers embedded in high purity alumina, and an electronic feedback circuit to control the power dissipated by these resistors, provides an ideal system for studying the kinetics of the solid-state reactions in thin films at temperatures between 300 and 1000 K. Because these devices serve both as heaters and thermometers, only two electrical leads into the vacuum chamber are necessary for their operation.

The as deposited Zr film is structurally unstable and heating it to the SSAR reaction temperature enables it to relax, thereby decreasing its resistance. The data in Fig. 7 shows that at 330°C, the rate of change in  $1/R$  decreases rapidly, approaching a saturation value after approximately 3 h. It is this rapid rate of change that makes it difficult to study the initial kinetics of the SSAR. Possible causes for the change in  $1/R$  include (a) recovery and/or recrystallization of the films, (b) relaxation of internal stresses in the films, and (c) annihilation of defects, such as mono- or di-vacancies, which are likely to be trapped into the films during condensation from the vapor phase. The total change in  $1/R$  for the zirconium film is approximately 1.5% whereas the initial increase in  $1/R$  for the Ni/Zr bilayer annealed at 350°C is approximately 2%. If the short-lived increase in  $1/R$  due to a structural relaxation in the zirconium film is superimposed onto the  $1/R$  change due to the SSAR, which is linear in  $t^{1/2}$ , the resultant  $1/R$  vs  $t^{1/2}$  curve would be similar to that shown in Fig. 6, which shows a maximum at very short reaction times. If the increase in  $1/R$  is weaker, as appears to be the case for lower reaction temperatures, then the measured  $1/R$  curve may not have a maximum but may instead appear as if there is a time delay for the onset of the reaction. The structural relaxation in the as-deposited films affects not only the initial stage of the SSAR; notice in Fig. 7 that at 330°C the relaxation continues for several hours, and thus should also affect, to a lesser degree, annealing stages (b) and (c).

The present measurements show that recovery affects the kinetics of SSARs in thin films. Researchers [9] have tried to circumvent structural relaxation effects in SSARs by depositing the thin films at the reaction temperatures. Because the time required for structural recovery is significantly longer than the deposition time, it is unlikely that these effects can be entirely eliminated. A comparison of the shape of the  $1/R$  curve within region (a) in Figs. 4 - 6 suggests that to minimize the recovery effects, the SSAR experiments should be made at the lowest possible temperature.

The transition from regimes (b) to (c) at time  $t_0$ , clearly seen in Fig. (5), as a discontinuity in the rate of change of  $1/R$ , corresponding to a slowing of the SSAR rate. The time to reach this transition depends on the thickness of the as-deposited films and on temperature. Notice, however, that the thicknesses of the as-deposited nickel and zirconium films greatly exceeds that which can be reacted by a SSAR ( $< 150$  nm, see Fig. 2), so that the exhaustion of one or both materials cannot be the cause for the decrease in the reaction. The temperature dependence of  $t_0$  suggests a diffusion-controlled process with activation energy of  $3 \text{ eV atom}^{-1}$ . This large activation energy rules out any possible participation of the nickel atoms, which have activation energies for diffusion in crystalline Zr and amorphous NiZr close to  $1 \text{ eV atom}^{-1}$ . The magnitude of the activation energy suggests a recovery process in the zirconium film controlled by self diffusion, which has an activation energy of  $2.77 \text{ eV}$  [25].

Although the present measurements show that recovery effects are important and can explain some of the features of the  $1/R$  versus  $t^{1/2}$  curves, it appears that additional mechanisms are required to explain the time delay for the initiation of the SSAR observed by van Rossum et al. [4] in Ni/Hf films using Rutherford backscattering techniques. This is because Rutherford measurements should be insensitive to the relaxation state of the films.

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## FIGURE CAPTIONS

Fig. 1 Resistance of a multilayer system of nickel and zirconium thin films during the continuous heating and cooling at  $10 \text{ K min}^{-1}$ . The cycle has been repeated twice. During the second cycle the resistance follows the line *f-g* traced during the cooling part of the first cycle.

Fig. 2 Resistance of three multilayer systems of nickel and zirconium thin films during the continuous heating and cooling at  $10 \text{ K min}^{-1}$ . The thickness of the films increases in proportion 1:2:4.

Fig. 3 Plot of  $\ln[x_{am}(dx_{am}/dt)]$  as a function of reciprocal temperature for the multilayers shown in Fig. 2. The straight line is a least-squares fit to the linear portions of curves 1x, 2x, and 4x.

Fig. 4. Change in electrical conductivity of a Ni-Zr bilayer annealed isothermally at  $300^\circ\text{C}$ .

Fig. 5. Change in electrical conductivity of a Ni-Zr bilayer annealed isothermally at  $315^\circ\text{C}$ .

Fig. 6. Change in electrical conductivity of a Ni-Zr bilayer annealed isothermally at  $350^\circ\text{C}$ .

Fig. 7. Change in electrical conductivity of a 400 nm-thick Zr film annealed isothermally at  $330^\circ\text{C}$ .

Fig. 8. Time  $t_0$  denoting the transition between annealing regimes (b) and (c) for the curves in Figs. 5 and 6, as a function of the square of the Zr layer thickness.

Fig. 9. Time  $t_0$  denoting the transition between annealing regimes (b) and (c) for the curves in Figs. 5 and 6, as a function of reciprocal temperature.

1.B.1

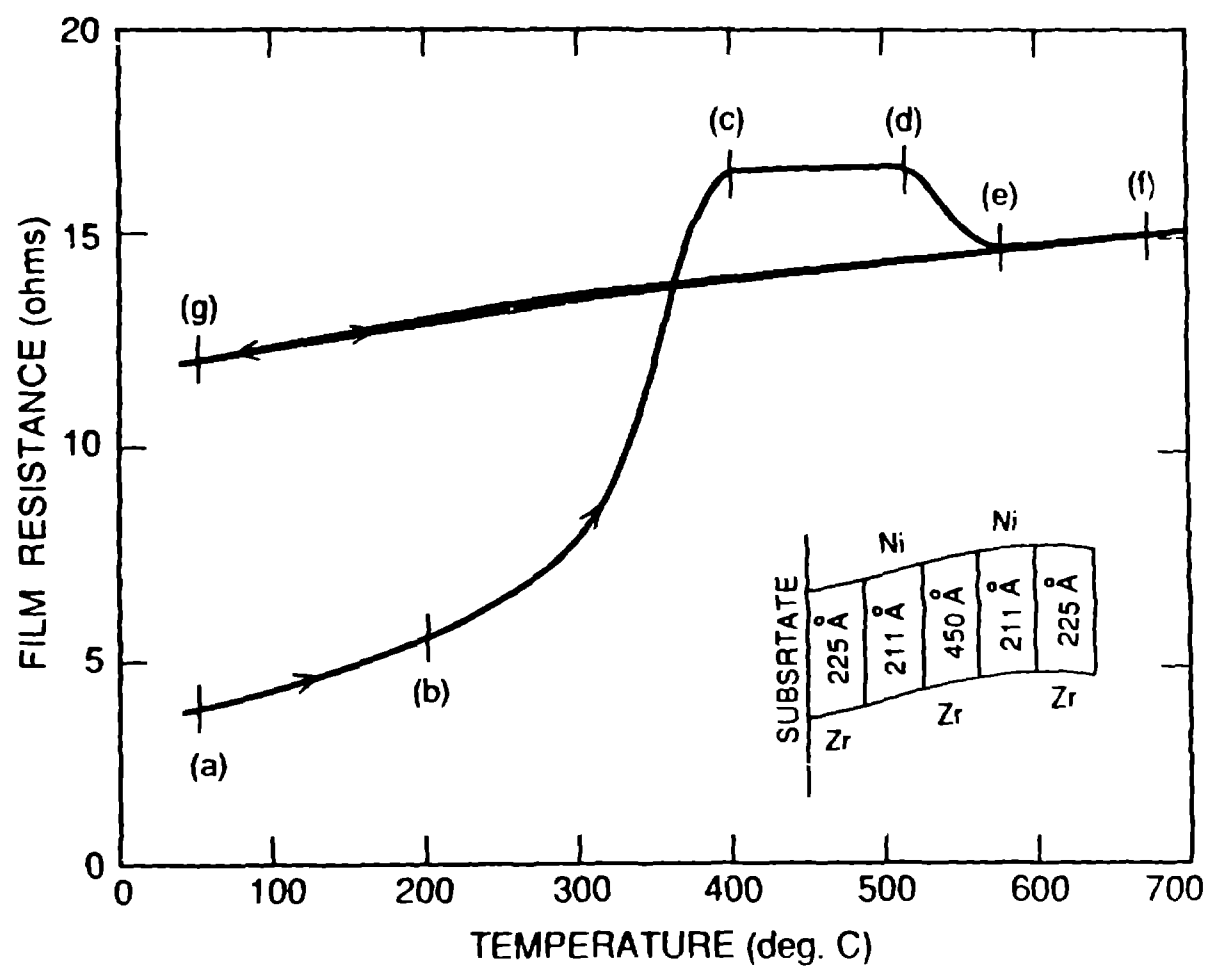


Fig. 2

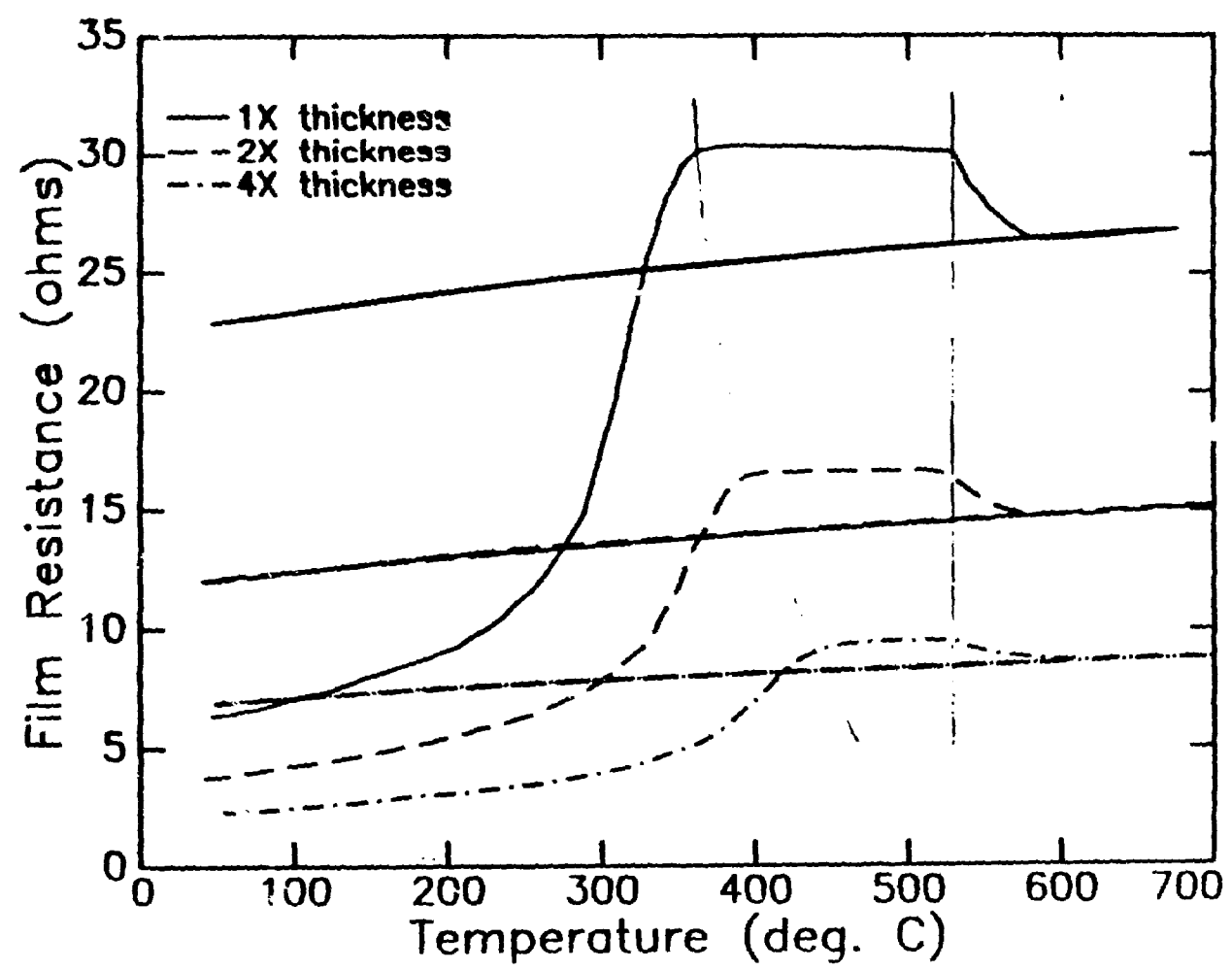


Fig. 3

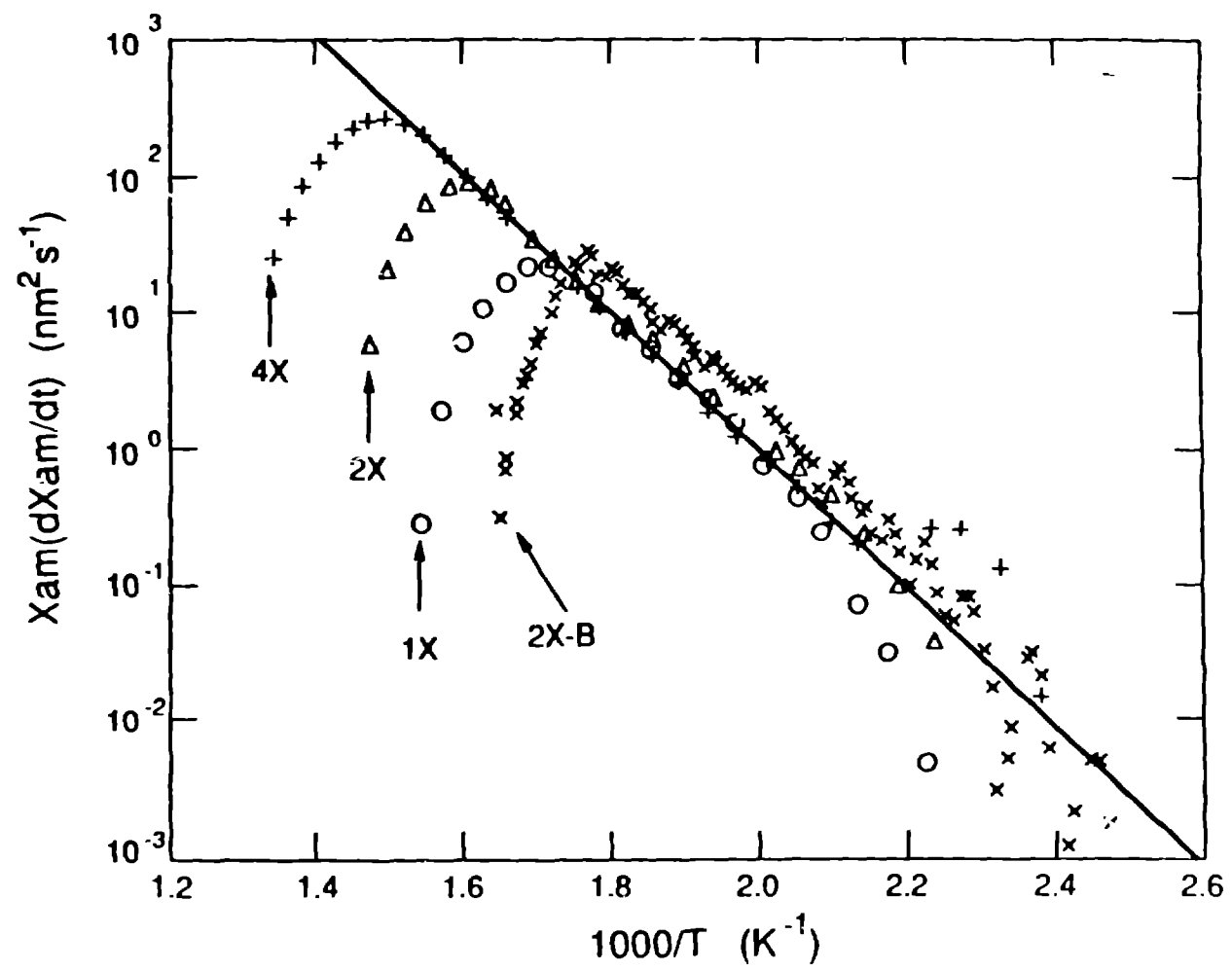


Fig. 4

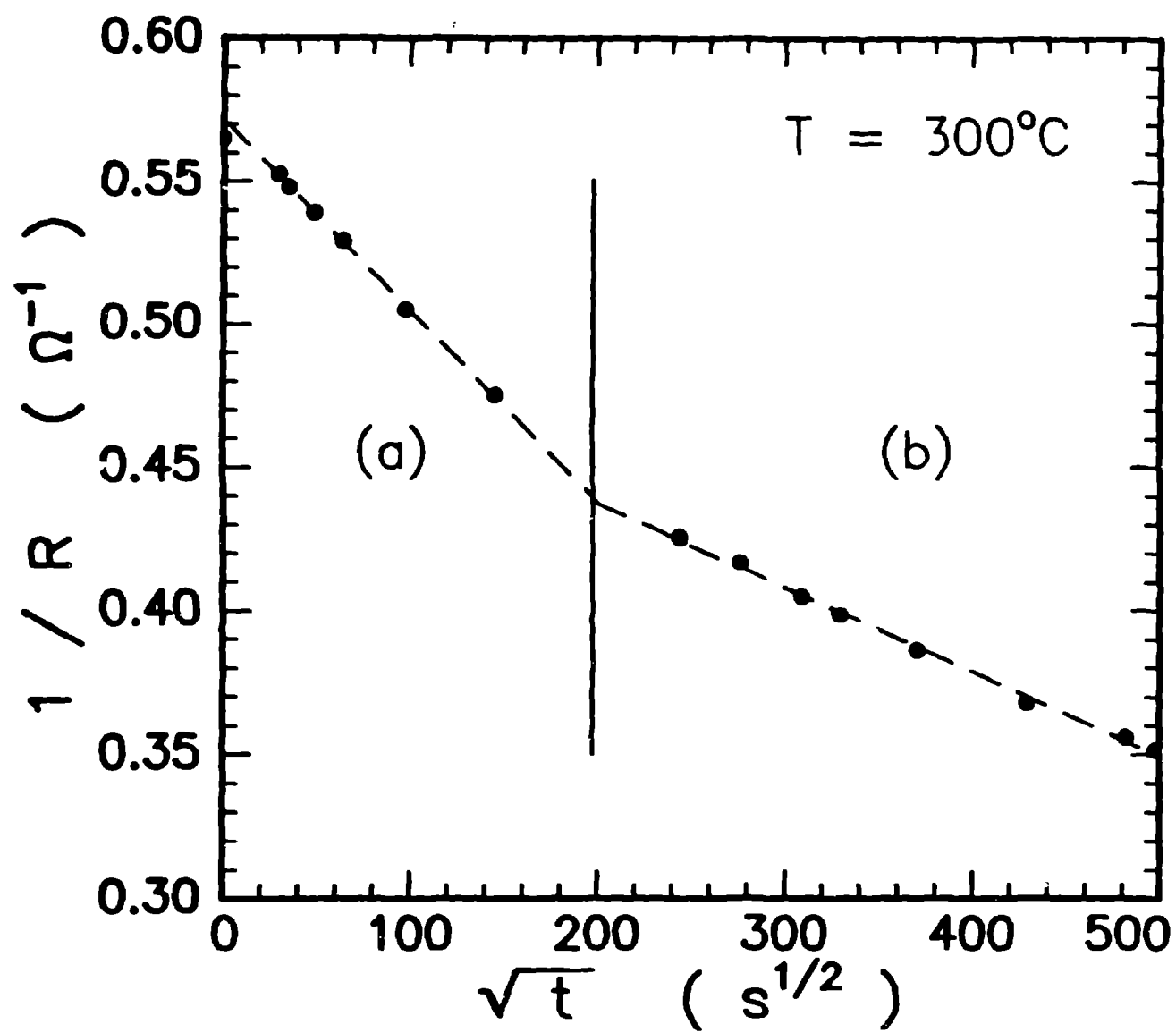


Fig. 5

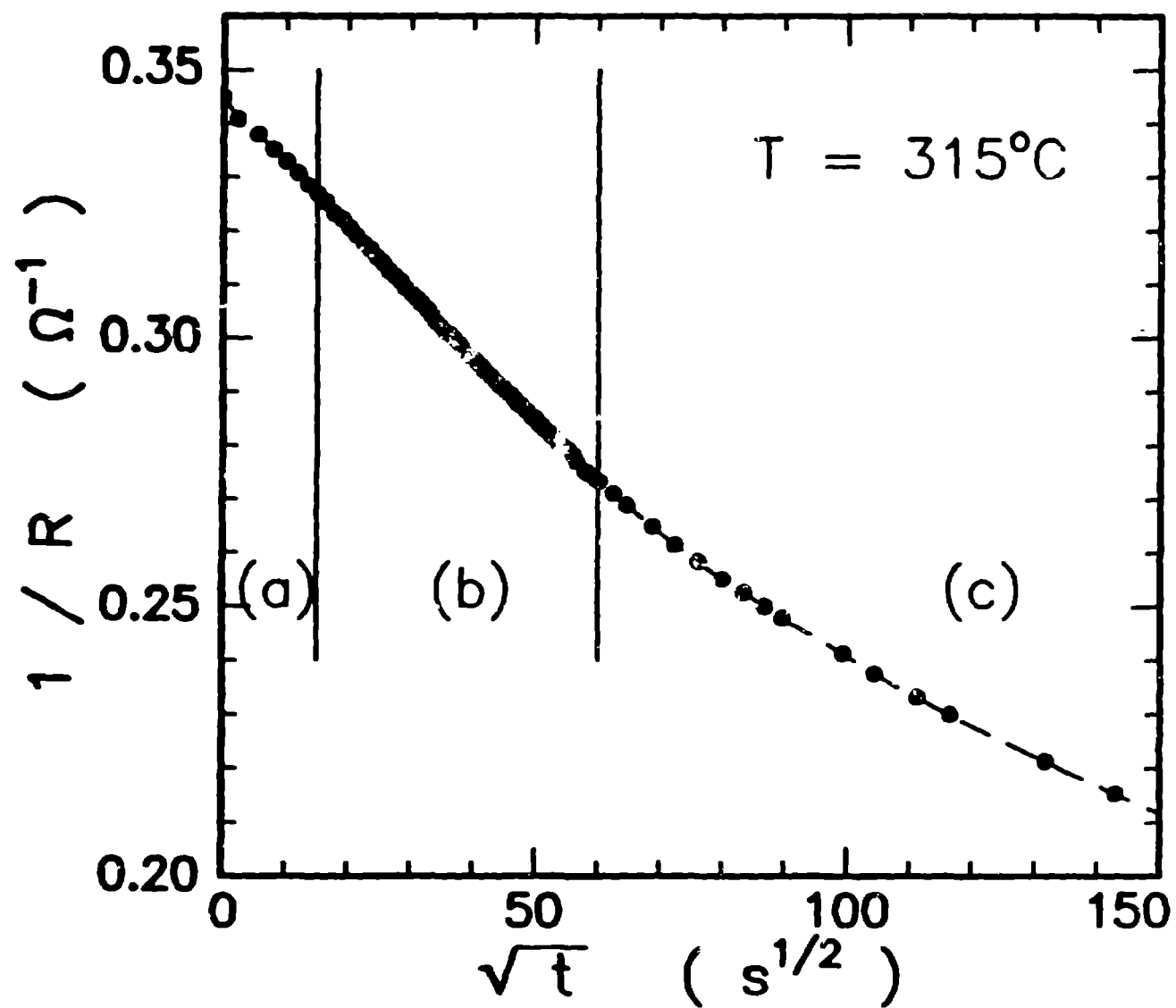
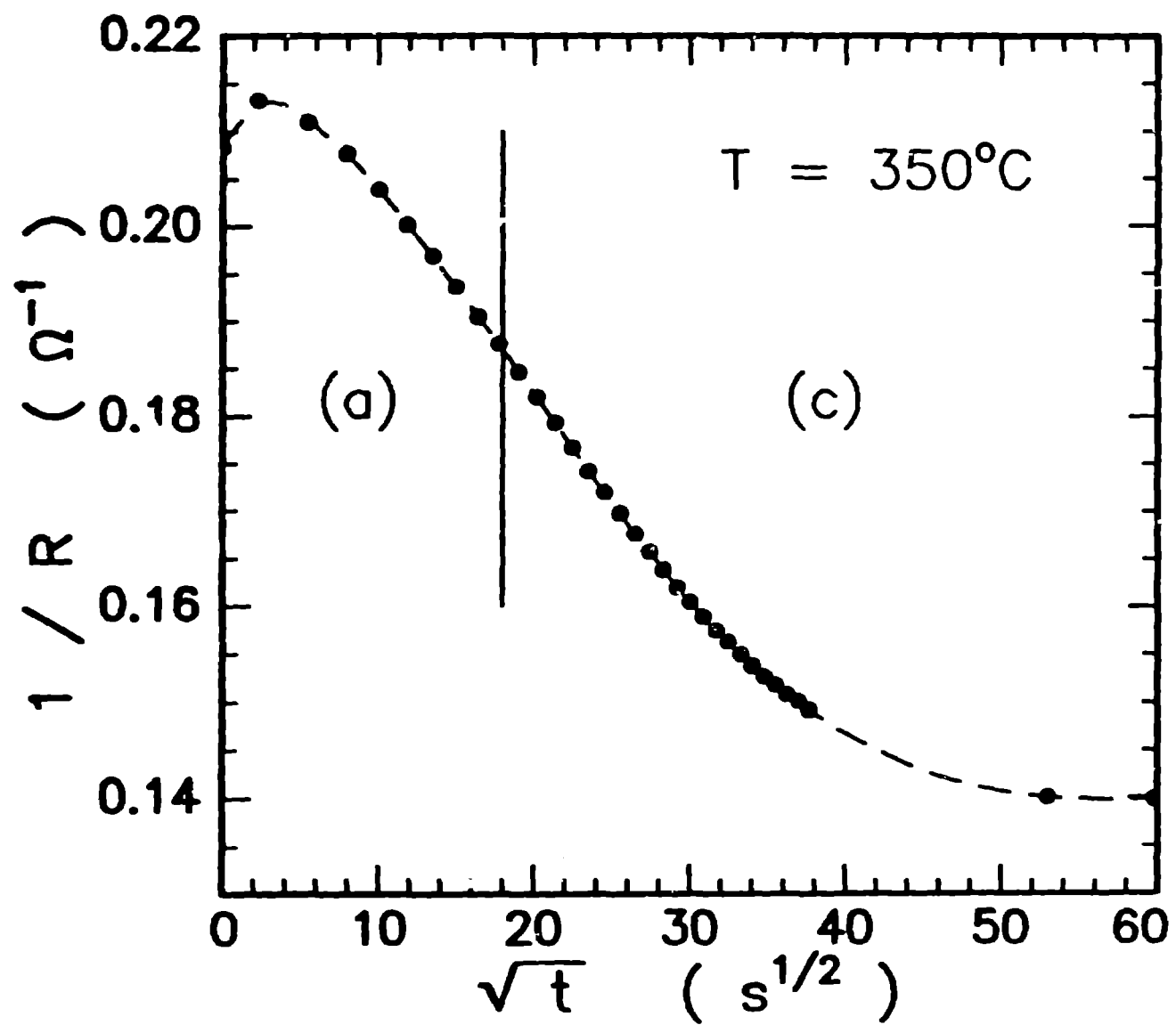


Fig. 6



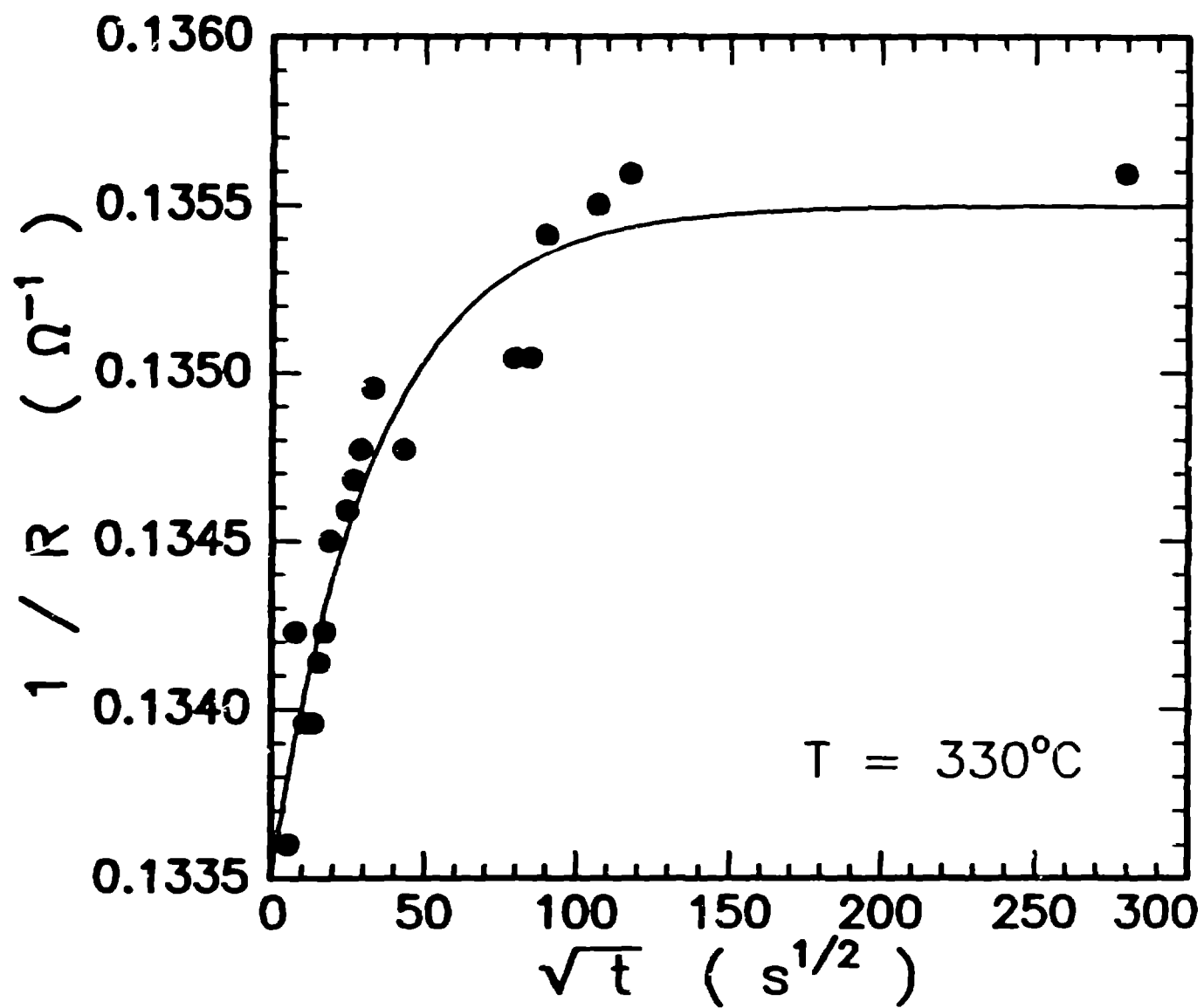


Fig. 7

Fig. 8

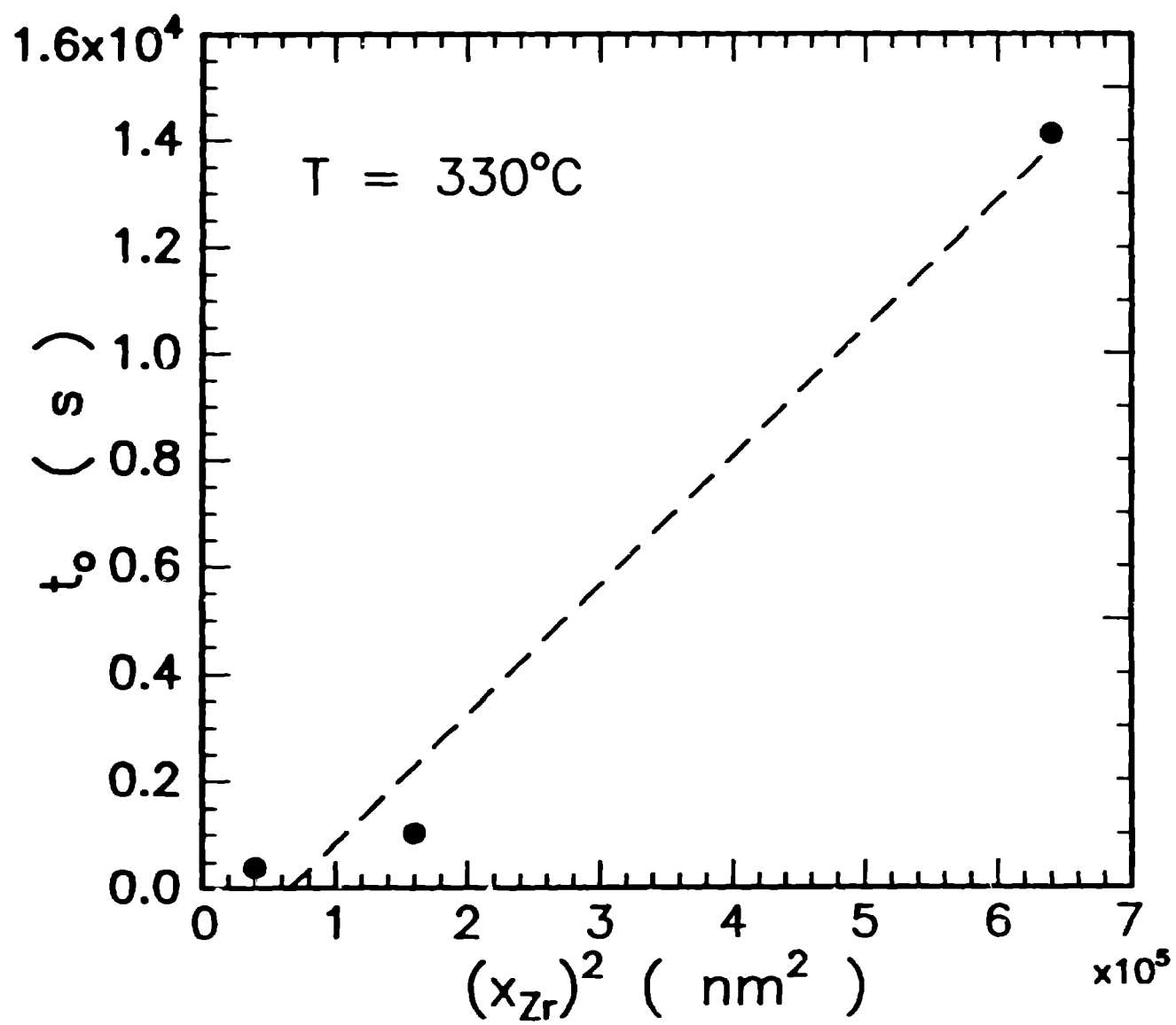


Fig. 9

